

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 546 690 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
04.03.1998 Bulletin 1998/10

(51) Int. Cl.<sup>6</sup>: C08F 4/642, C08F 10/00

(21) Application number: 92310315.4

(22) Date of filing: 12.11.1992

**(54) Catalyst components for polymerization of olefins**

Katalysatorbestandteile für Olefinpolymerisation

Composants de catalyseur pour polymérisation d'oléfines

(84) Designated Contracting States:  
DE FR GB NL

(30) Priority: 12.11.1991 JP 323848/91  
12.11.1991 JP 323849/91

(43) Date of publication of application:  
16.06.1993 Bulletin 1993/24

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EP-A- 0 260 130 EP-A- 0 447 071  
DE-A- 1 720 785 US-A- 5 021 382

Remarks:

The file contains technical information submitted  
after the application was filed and not included in  
this specification

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## Description

This invention relates to a process for the manufacture of olefinic polymers in the presence of a selected catalyst.

Catalyst compositions comprising zirconium compounds, typically metallocene and aluminoxane are known for use in the homopolymerization of olefins such as ethylene or the copolymerization of ethylene/alpha-olefins as disclosed for example in Japanese Laid-Open Patent Publication No. 58-19309. While the disclosed prior art process is advantageous so far as concerns the availability of polymerized products with increased yield, it has a drawback in that the polymers obtained have a relatively narrow distribution of molecular weight or composition, coupled with a relatively low molecular weight. When taking into account the molecular weight alone, it would be possible to increase the molecular weight of a polymer to some extent by making a proper selection of transition metals from among the group of metallocene.

The molecular weight of a polymer may be increased by the use of a transition metal compound having a 2,3 and 4-substituted cyclopentadienyl group as disclosed in Japanese Laid-Open Patent Publication No. 63-234005, or by the use of a hafnium compound having a ligand bonded to at least two cross-linked conjugated cycloalkadienyl groups as disclosed in Japanese Laid-Open Patent Publication No. 2-22307. However, such catalyst components are complicated if not difficult to synthesize. The use of hafnium compounds is not very conducive to polymer yields. The prior catalysts, often being soluble in the reaction system, are further disadvantageous in that the polymer resulting from the slurry or gas-phase polymerization would have reduced bulk density and deteriorated granular properties. Attempts have been made to produce a polymerisation catalyst which would produce polymer products having improved particle size and bulk density as disclosed in EP-A-0260130, the catalyst comprising a supported reaction product of a metallocene of a metal of Group IVB, VB or VIB of the periodic table, a non-metallocene compound of a metal of Group IVB, VB or VIB and an aluminoxane, said reaction product formed in the presence of a support material.

Attempts have also been made to develop a catalyst, as disclosed in EP-A1-1447071, which is suited to the heterogeneous process of polymerisation of olefins in suspensions or in gaseous phase. The disclosed catalyst consisting of spheroidal particles having a narrow particle size distribution and comprises of a support containing magnesium dichloride and an electron donor, free from labile hydrogen, a zirconium metallocene, at least one halide of titanium or vanadium and optionally an organoaluminium compound.

With the foregoing difficulties of the prior art in view, the present invention seeks to provide a process for the manufacture of polyolefins in the presence of a novel catalyst with increased yields, wherein the polyolefins have a relatively wide molecular weight distribution, a narrow composition distribution and improved granular quality.

This, and other objects and features of the invention, will appear clear from the following detailed description of certain preferred embodiments.

According to the invention, there is provided a process for the manufacture of polyolefins which comprises polymerizing an olefinic hydrocarbon selected from the group consisting of alpha-olefins, cyclic olefins, dienes, trienes and styrene analogs in the presence of a catalyst composition, said catalyst composition comprising a first component (I) and a second component (II),

said first component (I) resulting from the reaction of a compound (i) of the formula



wherein  $\text{R}^1$  is an alkyl, alkoxy, aryloxy or aralkyloxy group of 1 - 24 carbon atoms,  $\text{X}^1$  is a halogen atom,  $\text{Me}^1$  is a metal of the group of zirconium, titanium and hafnium, and  $n$  is an integer of  $0 \leq n \leq 4$ , in an amount by transition metal concentration of 0.01-500 millimoles per 100g of a carrier (iv) defined hereinafter;

a compound (ii) of the formula



wherein  $\text{R}^2$  is a hydrocarbon group of 1 - 24 carbon atoms,  $\text{X}^2$  is an alkoxy group of 1 - 12 carbon atoms or a halogen atom,  $\text{Me}^2$  is an element of Groups I-III in the Periodic Table,  $z$  is the valence of  $\text{Me}^2$ , and  $m$  is an integer of  $0 < m \leq Z$ , in an amount of 0.01-100 moles per mole of said compound (i);

an organocyclic compound (iii) in an amount of 0.01-10 moles per mole of said compound (i), said organocyclic compound being selected from the group consisting of cyclic hydrocarbons having 2 or more conjugated double bonds in the molecule and a carbon number of 4-24; a compound of the formula



wherein Cp is a cyclopentadienyl group,  $\text{R}^3$  is a hydrocarbon group of 1-24 carbon atoms,  $\text{X}^3$  is a halogen atom, and  $r$

and s are  $0 < s \leq 4$  and  $0 \leq s \leq 3$  respectively, and a compound of the formula



- 5 wherein Ind is an indenyl group,  $\text{R}^4$  is a hydrocarbon group of 1-24 carbon atoms,  $\text{X}^4$  is a halogen atom; and t and u are  $0 < t \leq 4$  and  $0 \leq u \leq 3$  respectively; and

an inorganic carrier and/or particulate polymer carrier (iv);

said second component (II) being a modified organoaluminium compound having Al-O-Al bonds derived from the reaction of an organoaluminium compound and water.

- 10 Figure 1 is a flow chart utilized to explain the process of preparing a catalyst used in the invention.

- The compound (i) which is used in the preparation of Component (I) of the inventive catalyst composition is represented by the formula  $\text{Me}^1 \text{R}^1_n \text{X}^1_{4-n}$  wherein  $\text{R}^1$  is a hydrocarbon moiety having a carbon atom number of from 1 to 24, preferably from 1 to 8, including an alkyl group such as methyl, ethyl, propyl, butyl, pentyl, hexyl and octyl, an alkenyl group such as vinyl and allyl, an aryl group such as phenyl, tolyl and xylyl, an aralkyl group such as benzyl, phenethyl, styryl and neophyl, an alkoxy group such as methoxy, ethoxy, propoxy, butoxy and pentyloxy, an aryloxy group such as phenoxy and tolyloxy, and an aralkyloxy group such as benzyloxy.  $\text{X}^1$  in the formula is a halogen atom such as fluorine, iodine, chlorine and bromine.  $\text{Me}^1$  is titanium, zirconium or hafnium, zirconium being preferred. n is  $0 \leq n \leq 4$ , preferably  $0 < n \leq 4$ .

- Specific examples of the compound (i) include tetramethyl zirconium, tetraethyl zirconium, tetrapropyl zirconium, tetra-n-butyl zirconium, tetrapentyl zirconium, tetraphenyl zirconium, tetratolyl zirconium, tetrabenzyl zirconium, tetramethoxy zirconium, tetraethoxy zirconium, tetrapropoxy zirconium, tetrabutoxy zirconium, tetraphenoxy zirconium, tetratolyloxy zirconium, tetrapentyloxy zirconium, tetrabenzyloxy zirconium, tetraallyl zirconium, tetraneophyl zirconium, trimethylmonochlorozirconium, triethylmonochlorozirconium, tripropylmonochlorozirconium, tri-n-butylmonochlorozirconium, tribenzylmonochlorozirconium, dimethyldichlorozirconium, diethyldichlorozirconium, di-n-butylidichlorozirconium, dibenzylidichlorozirconium, monomethyltrichlorozirconium, monoethyltrichlorozirconium, mono-n-butyltrichlorozirconium, monobenzyltrichlorozirconium, tetrachlorozirconium, tetramethoxyzirconium, trimethoxymonochlorozirconium, dimethoxydichlorozirconium, monomethoxytrichlorozirconium, tetraethoxyzirconium, triethoxymonochlorozirconium, diethoxydichlorozirconium, monoethoxytrichlorozirconium, tetraisopropoxyzirconium, triisopropoxymonochlorozirconium, diisopropoxydichlorozirconium, monoisopropoxytrichlorozirconium, tetra-n-butoxyzirconium, tri-n-butoxymonochlorozirconium, di-n-butoxydichlorozirconium, mono-n-butoxytrichlorozirconium, tetrapentoxyzirconium, tri-pentoxymonochlorozirconium, dipentoxydichlorozirconium, monopentoxytrichlorozirconium, tetraphenoxyzirconium, triphenoxymonochlorozirconium, diphenoxydichlorozirconium, monophenoxytrichlorozirconium, tetratolyloxyzirconium, tritolyloxymonochlorozirconium, ditolyoxydichlorozirconium, monotolyoxytrichlorozirconium, tetrabenzyloxyzirconium, tribenzyloxymonochlorozirconium, dibenzyloxydichlorozirconium, monobenzylxyloxytrichlorozirconium, trimethylmonobromozirconium, triethylmonobromozirconium, tripropylmonobromozirconium, tri-n-butylmonobromozirconium, tribenzylmonobromozirconium, dimethyldibromozirconium, diethyldibromozirconium, di-n-butylidibromozirconium, dibenzylidibromozirconium, monomethyltribromozirconium, monoethyltribromozirconium, mono-n-butyltribromozirconium, monobenzyltribromozirconium, tetrobromozirconium, trimethoxymonobromozirconium, dimethoxydibromozirconium, monomethoxytribromozirconium, triethoxymonobromozirconium, diethoxydibromozirconium, monoethoxytribromozirconium, triisopropoxymonobromozirconium, diisopropoxydibromozirconium, monoisopropoxytribromozirconium, tri-n-butoxymonobromozirconium, di-n-butoxydibromozirconium, mono-n-butoxytribromozirconium, tri-pentoxymonobromozirconium, dipentoxydibromozirconium, monopentoxytribromozirconium, triphenoxymonobromozirconium, diphenoxydibromozirconium, monophenoxytribromozirconium, tritolyloxymonobromozirconium, ditolyoxydibromozirconium, monotolyoxytribromozirconium, tribenzyloxymonobromozirconium, dibenzyloxydibromozirconium, monobenzylxyloxytribromozirconium, trimethylmonoiodozirconium, triethylmonoiodozirconium, tripropylmonoiodozirconium, tri-n-butylmonoiodozirconium, tribenzylmonoiodozirconium, dimethyldiiodozirconium, diethyldiiodozirconium, dipropyldiiodozirconium, di-n-butylidiodozirconium, dibenzylidiodozirconium, monomethyltriiodozirconium, monoethyltriiodozirconium, monopropyltriiodozirconium, mono-n-butyltriiodozirconium, monobenzyltriiodozirconium, tetraiodozirconium, trimethoxymonoiodozirconium, dimethoxydiiodozirconium, monomethoxytriiodozirconium, triethoxymonoiodozirconium, diethoxydiiodozirconium, monoethoxytriiodozirconium, triisopropoxymonoiodozirconium, diisopropoxydiiodozirconium, monoisopropoxytriiodozirconium, tri-n-butoxymonoiodozirconium, di-n-butoxydiiodozirconium, mono-n-butoxytriiodozirconium, tri-pentoxymonoiodozirconium, dipentoxydiiodozirconium, monopentoxytriiodozirconium, triphenoxymonoiodozirconium, diphenoxydiiodozirconium, monophenoxytriiodozirconium, tritolyloxymonoiodozirconium, ditolyoxydiiodozirconium, monotolyoxytriiodozirconium, tribenzyloxymonoiodozirconium, dibenzyloxydiiodozirconium, monobenzylxyloxytriiodozirconium, tribenzylmonomethoxyzirconium, tribenzylmonoethoxyzirconium, tribenzylmonopropoxyzirconium, tribenzylmonobutoxizirconium, tribenzylmonophenoxyzirconium, dibenzylmethoxyzirconium, dibenzyl-diethoxyzirconium, dibenzyl-dipropoxyzirconium, dibenzyl-dibutoxizirconium, dibenzyl-diphenoxyzirconium, monobenzyltrimethoxyzirconium,

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 ophyl titanium, trimethylmonochlorotitanium, triethylmonochlorotitanium, tripropylmonochlorotitanium, tri-n-butylmono-  
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tri-n-butoxymonochlorohafnium, di-n-butoxydichlorohafnium, mono-n-butoxytrichlorohafnium, tetrapentoxylhafnium, tripentoxymonochlorohafnium, dipentoxydichlorohafnium, monopentoxytrichlorohafnium, tetraphenoxylhafnium, triphenoxymonochlorohafnium, diphenoxydichlorohafnium, monophenoxytrichlorohafnium, tetratoloxylhafnium, tritoloxymonochlorohafnium, ditoloxydichlorohafnium, monotoloxyltrichlorohafnium, tetrabenzylloxylhafnium, tribenzylloxymonochlorohafnium, dibenzylloxydichlorohafnium, monobenzylloxyltrichlorohafnium, trimethylmonobromohafnium, triethylmonobromohafnium, tripropylmonobromohafnium, tri-n-butylmonobromohafnium, tribenzylmonobromohafnium, dimethyldibromohafnium, diethyldibromohafnium, di-n-butylmonobromohafnium, dibenzylmonobromohafnium, monomethyltribromohafnium, monoethyltribromohafnium, mono-n-butyltribromohafnium, monobenzyltribromohafnium, tetrobromohafnium, trimethoxymonobromohafnium, dimethoxydibromohafnium, monomethoxytribromohafnium, triethoxymonobromohafnium, diethoxydibromohafnium, monoethoxytribromohafnium, triisopropoxymonobromohafnium, diisopropoxydibromohafnium, monoisopropoxytribromohafnium, tri-n-butoxymonobromohafnium, di-n-butoxydibromohafnium, mono-n-butoxytribromohafnium, tripentoxymonobromohafnium, dipentoxydibromohafnium, monopentoxytribromohafnium, triphenoxymonobromohafnium, diphenoxydibromohafnium, monophenoxytribromohafnium, tritoloxymonobromohafnium, ditoloxydibromohafnium, monotoloxyltribromohafnium, tribenzloxymonobromohafnium, dibenzloxyltribromohafnium, monobenzloxyltribromohafnium, trimethylmonoiodobromohafnium, triethylmonoiodobromohafnium, tripropylmonoiodobromohafnium, tri-n-butylmonoiodobromohafnium, tribenzylmonoiodobromohafnium, dimethyldiiodobromohafnium, diethyldiiodobromohafnium, dipropyldiiodobromohafnium, di-n-butylmonoiodobromohafnium, dibenzylmonoiodobromohafnium, monomethyltriiodobromohafnium, monoethyltriiodobromohafnium, monopropyltriiodobromohafnium, mono-n-butyltriiodobromohafnium, monobenzyltriiodobromohafnium, tetraiodobromohafnium, trimethoxymonoiodobromohafnium, dimethoxydiiodobromohafnium, monomethoxytriiodobromohafnium, triethoxymonoiodobromohafnium, diethoxydiiodobromohafnium, monoethoxytriiodobromohafnium, triisopropoxymonoiodobromohafnium, diisopropoxydiiodobromohafnium, monoisopropoxytriiodobromohafnium, tri-n-butoxymonoiodobromohafnium, di-n-butoxydiiodobromohafnium, mono-n-butoxytriiodobromohafnium, tripentoxymonoiodobromohafnium, dipentoxydiiodobromohafnium, monopentoxytriiodobromohafnium, triphenoxymonoiodobromohafnium, diphenoxydiiodobromohafnium, monophenoxytriiodobromohafnium, tritoloxymonoiodobromohafnium, ditoloxydiiodobromohafnium, monotoloxyltriiodobromohafnium, tribenzloxymonoiodobromohafnium, dibenzylmonoiodobromohafnium, monobenzylmonoiodobromohafnium, tribenzylmonobutoxyhafnium, tribenzylmonophenoxyhafnium, dibenzylmethoxyhafnium, dibenzylmethoxyhafnium, dibenzylpropoxyhafnium, dibenzylbutoxyhafnium, dibenzylphenoxyhafnium, monobenzyltrimethoxyhafnium, monobenzyltriethoxyhafnium, monobenzyltripropoxyhafnium, monobenzyltributoxyhafnium, monobenzyltriphenoxyhafnium, trineophylmonomethoxyhafnium, trineophylmonoethoxyhafnium, trineophylmonopropoxyhafnium, trineophylmonobutoxyhafnium, trineophylmonophenoxyhafnium, dineophyldimethoxyhafnium, dineophyldiethoxyhafnium, dineophyldipropoxyhafnium, dineophyldibutoxyhafnium, dineophyldiphenoxyhafnium, mononeophyltrimethoxyhafnium, mononeophyltriethoxyhafnium, mononeophyltripropoxyhafnium, mononeophyltributoxyhafnium, mononeophyltriphenoxyhafnium and the like, most preferred of which compounds are tetramethylzirconium tetraethylzirconium, tetrabenzylzirconium, tetrapropylzirconium, tetrabutoxylzirconium and tetrachlorozirconium.

The compound (ii) used in the invention is represented by the formula  $\text{Me}^2\text{R}_m^2\text{X}_m^2$  wherein  $\text{R}^2$  is a hydrocarbon group having a carbon number of from 1 to 24, preferably from 1 to 12, more preferably from 1 to 8, including an alkyl group such as methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, octyl, decyl and dodecyl, an alkenyl group such as vinyl and allyl, an aryl group such as phenyl, tolyl and xylyl, and an aralkyl group such as benzyl, phenethyl and styryl;  $\text{X}^2$  is an alkoxy group, of 1 - 12 carbon atoms, preferably 1 - 6 carbon atoms such as methoxy, ethoxy, propoxy and butoxy, or a halogen atom such as fluorine, iodine, chlorine and bromine;  $\text{Me}^2$  is an element of Groups I - III in the Periodic Table; Z is a valence of  $\text{Me}^2$ ; and m is an integer of  $0 < m \leq Z$ .

Specific examples of the compound (ii) eligible for the purpose of the invention are methyl lithium, ethyl lithium, n-propyllithium, isopropyllithium, n-butyllithium, t-butyllithium, pentyllithium, octyllithium, phenyllithium, benzyl lithium, dimethylmagnesium, diethylmagnesium, di-n-propylmagnesium, diisopropylmagnesium, di-n-butylmagnesium, di-t-butylmagnesium, dipentylmagnesium, methylmagnesium chloride, n-propylmagnesium chloride, isopropylmagnesium chloride, n-butylmagnesium chloride, t-butylmagnesium chloride, pentylmagnesium chloride, octylmagnesium chloride, phenylmagnesium chloride, benzylmagnesium chloride, methylmagnesium bromide, methylmagnesium iodide, ethylmagnesium bromide, ethylmagnesium iodide, n-propylmagnesium bromide, n-propylmagnesium iodide, isopropylmagnesium bromide, isopropylmagnesium iodide, n-butylmagnesium bromide, n-butylmagnesium iodide, t-butylmagnesium bromide, t-butylmagnesium iodide, pentylmagnesium bromide, pentylmagnesium iodide, octylmagnesium bromide, octylmagnesium iodide, phenylmagnesium bromide, phenylmagnesium iodide, benzylmagnesium bromide, benzylmagnesium iodide, dimethylzinc, diethylzinc, di-n-propylzinc, diisopropylzinc, di-n-butylzinc, di-t-butylzinc, dipentylzinc, dioctylzinc, diphenylzinc, dibenzylzinc, trimethylboron, triethylboron, tri-n-propylboron, triisopropylboron, tri-n-butylboron, tri-t-butylboron, triphenylboron, triethylboron, tripropylboron, triphenylboron and tribenzylboron.

The compound (ii) further includes an organoaluminum compound of the formulae  $\text{R}_3\text{Al}$ ,  $\text{R}_2\text{AlX}$ ,  $\text{RAlX}_2$ ,  $\text{RAl(OR)X}$  and  $\text{R}_3\text{Al}_2\text{X}_3$  wherein R is a hydrocarbon group and X is a halogen atom, specific examples of which include trimethylaluminum, triethylaluminum, diethylaluminum chloride, diethylaluminum bromide, diethylaluminum fluoride, diethylaluminum iodide, ethylaluminum dichloride, ethylaluminum dibromide, ethylaluminum difluoride ethylaluminum diiodide,

tripropylaluminum, dipropylaluminum chloride, dipropylaluminum bromide, dipropylaluminum fluoride dipropylaluminum iodide, propylaluminum dichloride, propylaluminum dibromide, propylaluminum difluoride propylaluminum diiodide, triisopropylaluminum, diisopropylaluminum chloride, diisopropylaluminum bromide, diisopropylaluminum fluoride, diisopropylaluminum iodide, ethylaluminum sesquichloride, ethylaluminum sesquibromide, propylaluminum sesquichloride, propylaluminum sesquibromide, n-butylaluminum sesquichloride, n-butylaluminum sesquibromide, isopropylaluminum dichloride, isopropylaluminum dibromide, isopropylaluminum difluoride, isopropylaluminum diiodide, tributylaluminum, dibutylaluminum chloride, dibutylaluminum bromide, dibutylaluminum fluoride, dibutylaluminum iodide, butylaluminum dichloride, butylaluminum dibromide, butylaluminum difluoride, butylaluminum diiodide, tri-sec-butylaluminum, di-sec-butylaluminum chloride, di-sec-butylaluminum bromide, di-sec-butylaluminum fluoride, di-sec-butylaluminum iodide, sec-butylaluminum dichloride, sec-butylaluminum dibromide, sec-butylaluminum difluoride, sec-butylaluminum diiodide, tri-tert-butylaluminum, di-tert-butylaluminum chloride, di-tert-butylaluminum bromide, di-tert-butylaluminum fluoride, di-tert-butylaluminum iodide, tert-butylaluminum dichloride, tert-butylaluminum dibromide, tert-butylaluminum difluoride, tert-butylaluminum diiodide, triisobutylaluminum, diisobutylaluminum chloride, diisobutylaluminum bromide, diisobutylaluminum fluoride, diisobutylaluminum iodide, isobutylaluminum dichloride, isobutylaluminum dibromide, isobutylaluminum difluoride, isobutylaluminum diiodide, trihexylaluminum, dihexylaluminum chloride, dihexylaluminum bromide, dihexylaluminum fluoride, dihexylaluminum iodide, hexylaluminum dichloride, hexylaluminum dibromide, hexylaluminum difluoride, hexylaluminum diiodide, tripentylaluminum, dipentylaluminum chloride, dipentylaluminum bromide, dipentylaluminum fluoride, dipentylaluminum iodide, pentylaluminum dichloride, pentylaluminum dibromide, pentylaluminum difluoride, pentylaluminum diiodide, methylaluminum methoxide, methylaluminum ethoxide, methylaluminum propoxide, methylaluminum butoxide, dimethylaluminum methoxide, dimethylaluminum ethoxide, dimethylaluminum propoxide, dimethylaluminum butoxide, ethylaluminum methoxide, ethylaluminum ethoxide, ethylaluminum propoxide, ethylaluminum butoxide, diethylaluminum methoxide, diethylaluminum ethoxide, diethylaluminum propoxide, diethylaluminum butoxide, propylaluminum methoxide, propylaluminum ethoxide, propylaluminum propoxide, propylaluminum butoxide, dipropylaluminum methoxide, dipropylaluminum ethoxide, dipropylaluminum propoxide, dipropylaluminum butoxide, butylaluminum methoxide, butylaluminum ethoxide, butylaluminum propoxide, butylaluminum butoxide, dibutylaluminum ethoxide, dibutylaluminum propoxide, dibutylaluminum butoxide and the like.

The compound (iii) is an organocyclic compound having two or more conjugated double bonds, examples of which include a cyclic hydrocarbon compound having two or more, preferably 2 - 4, more preferably 2 - 3 conjugated double bonds and a carbon number of 4 - 24, preferably 4 - 12 in the molecule such as an aralkylene of 7 - 24 carbon atoms, cyclopentadiene, substituted cyclopentadiene, indene, substituted indene, fluorene, substituted fluorene, cycloheptatriene, substituted cycloheptatriene, cyclooctatetraene and substituted cyclooctatetraene. Each of such substituted compounds has a substituting group such as alkyl or aralkyl of 1 - 12 carbon atoms.

Specific examples of the compound (iii) include cyclopentadiene, methylcyclopentadiene, ethylcyclopentadiene, t-butylcyclopentadiene, hexylcyclopentadiene, octylcyclopentadiene, 1,2-dimethylcyclopentadiene, 1,3-dimethylcyclopentadiene, 1,2,4-trimethylcyclopentadiene, 1,2,3,4-tetramethylcyclopentadiene, pentamethylcyclopentadiene, indene, 4-methyl-1-indene, 4,7-dimethylindene, 4,5,6,7-tetrahydroindene, fluorene, methylfluorene, cycloheptatriene, methylcycloheptatriene, cyclooctatetraene and methylcyclooctatetraene. These compounds may be bonded through the medium of an alkylene group of 2 - 8, preferably 2 - 3 carbon atoms, such bonded compounds including for example bis-indenylethane, bis(4,5,6,7-tetrahydro-1-indenyl)ethane, 1,3-propanedimethyl-bis(4,5,6,7-tetrahydro)indene, propylene-bis(1-indene), isopropyl(1-indenyl) cyclopentadiene, diphenylmethylen(9-fluorenyl) cyclopentadiene and isopropylcyclopentadienyl-1-fluorene.

Another class of eligible compound (iii) according to the invention is represented by the formula



wherein Cp is a cyclopentadienyl group;  $\text{R}^3$  is a hydrocarbon group of 1 - 24, preferably 1 - 12 carbon atoms including an alkyl group such as methyl, ethyl, propyl, butyl, pentyl, hexyl and octyl, an alkenyl group such as vinyl and allyl, an aryl group such as phenyl, tolyl and xyl, and an aralkyl group such as benzyl, phenethyl, styryl and neophyl;  $\text{X}^3$  is a halogen atom including fluorine, iodine, chlorine and bromine; and r and s are  $0 < r \leq 4$  and  $0 \leq s \leq 3$  respectively.

Specific examples of the above compound (iii) include monocyclopentadienyl silane, dicyclopentadienyl silane, tricyclopentadienyl silane, tetracyclopentadienyl silane, monocyclopentadienylmonomethyl silane, monocyclopentadienylmonoethyl silane, monocyclopentadienyldimethyl silane, monocyclopentadienyldiethyl silane, monocyclopentadienyltrimethyl silane, monocyclopentadienyltriethyl silane, monocyclopentadienylmonomethoxy silane, monocyclopentadienylmonoethoxy silane, monocyclopentadienylmonophenoxy silane, monocyclopentadienylmonomethylmonochloro silane, monocyclopentadienylmonoethylmonochloro silane, monocyclopentadienylmonomethyldichloro silane, monocyclopentadienylmonoethyldichloro silane, monocyclopentadienyltrichloro silane, dicyclopentadienyldimethyl silane, dicyclopentadienyldiethyl silane, dicyclopentadienylmethylethyl silane, dicyclopentadienyldipropyl silane, dicyclopentadienylethylpropyl silane, dicyclopentadienyldiphenyl silane, dicyclopentadienylmeth-

ylphenyl silane, dicyclopentadienylmethylchloro silane, dicyclopentadienylethylchloro silane, dicyclopentadienyldichloro silane, dicyclopentadienylmonomethoxy silane, dicyclopentadienylmonoethoxy silane, dicyclopentadienylmonomethoxymonochloro silane, dicyclopentadienylmonoethoxymonochloro silane, tricyclopentadienylmonomethyl silane, tricyclopentadienylmonoethyl silane, tricyclopentadienylmonomethoxy silane, tricyclopentadienylmonoethoxy silane and tricyclopentadienylmonochloro silane.

A further eligible compound (iii) is represented by the formula



wherein Ind is an indenyl group;  $\text{R}^4$  is a hydrocarbon group of 1 - 24, preferably 1 - 12 carbon atoms including an alkyl group such as methyl, ethyl, propyl, butyl, pentyl, hexyl and octyl, an alkenyl group such as vinyl and allyl, an aryl group such as phenyl, tolyl and xylyl, and an aralkyl group such as benzyl, phenethyl, styryl and neophyl;  $\text{X}^4$  is a halogen atom including fluorine, iodine, chlorine and bromine; and t and u are  $0 < t \leq 4$  and  $0 \leq u \leq 3$  respectively.

Specific examples of the above compound (iii) include monoindenyl silane, diindenyl silane, triindenyl silane, tetraindenyl silane, monoindenylmonomethyl silane, monoindenylmonoethyl silane, monoindenyldimethyl silane, monoindenyl-diethyl silane, monoindenyltriethyl silane, monoindenylmonomethoxy silane, monoindenylmonoethoxy silane, monoindenylmonophenoxy silane, monoindenylmonomethylmonochloro silane, monoindenylmonoethylmonochloro silane, monoindenylmonomethyldichloro silane, monoindenylmonoethyldichloro silane, monoindenyltrichloro silane, bisindenyl-dimethyl silane, bisindenyl-diethyl silane, bisindenylmethyl-ethyl silane, bisindenyl-dipropyl silane, bisindenyl-diphenyl silane, bisindenylmethyl-phenyl silane, bisindenylmethyl-chloro silane, bisindenylethyl-chloro silane, bisindenyl-dichloro silane, bisindenylmonomethoxy silane, bisindenylmonoethoxy silane, bisindenylmonomethoxymonochloro silane, bisindenylmonoethoxymonochloro silane, triindenylmonoethyl silane, triindenylmonoethoxy silane, triindenylmonomethoxy silane, triindenylmonochloro silane.

An inorganic carrier and/or particulate polymer carrier is used as component (iv) of the catalyst composition. The inorganic carrier may be intrinsically in the form of particles, granules, flakes, foil or fibers, but, whatever the shape may be, should be 5 - 200  $\mu\text{m}$ , preferably 10 - 100  $\mu\text{m}$  in maximum length. The inorganic carrier is preferably porous, having a surface area of 5 - 1,000  $\text{m}^2/\text{g}$  and a pore volume of 0.05 - 3  $\text{cm}^3/\text{g}$ . It may be chosen from the group of a carbonaceous material, a metal, a metal oxide, a metal chloride and a metal carbonate, or a mixture thereof, which is calcined usually at 200° - 900°C in the air, nitrogen, argon or other inert gas. Suitable metals for the inorganic carrier (iii) are aluminum and nickel. Eligible metal oxides are Group I - VIII metal oxides of the Periodic Table including  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{B}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3 \cdot \text{MgO}$ ,  $\text{Al}_2\text{O}_3 \cdot \text{CaO}$ ,  $\text{Al}_2\text{O}_3 \cdot \text{MgO} \cdot \text{CaO}$ ,  $\text{Al}_2\text{O}_3 \cdot \text{MgO} \cdot \text{SiO}_2$ ,  $\text{Al}_2\text{O}_3 \cdot \text{CuO}$ ,  $\text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3 \cdot \text{NiO}$  and  $\text{SiO}_2 \cdot \text{MgO}$ . The double oxides are not particularly restricted in terms of structure and component ratio when used in the invention. The metal oxides may have adsorbed thereto small quantities of moisture and may further contain a small amount of impurities.

The metal chloride used in the invention is a chloride of an alkaline metal or alkaline earth metal, preferably  $\text{MgCl}_2$  and  $\text{CaCl}_2$ . Examples of the metal carbonate are magnesium carbonate, calcium carbonate and barium carbonate, while those of the carbonaceous material referred to herein are carbonblack and activated carbon. The above metal oxides are most preferred amongst the other inorganic carrier materials.

The term particulate polymer as used herein as a catalyst support or carrier (iv) designates a solid particulate form of either thermoplastic or thermosetting resin having an average particle size 5 - 2,000  $\mu\text{m}$ , preferably 10 - 100  $\mu\text{m}$ , practically ranging from low molecular weight to ultra high molecular weight polymers as long as these polymers remain solid during the stages of catalyst preparation and polymerization reaction. Specific examples of the particulate polymer include ethylene polymers, ethylene alpha-olefin copolymers, propylene polymers or copolymers, poly-1-butene and like polyolefins preferably of 2 - 12 carbon atoms, polyester, polyamide, polyvinylchloride, polymethylacrylate, polymethylmethacrylate, polystyrene, polynorbornen and naturally occurring polymers as well as mixtures thereof. The foregoing inorganic and particulate polymer carriers may be used per se as component (iv) according to the invention. Alternatively, they may be pretreated with an organoaluminum compound such as trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, dimethylaluminum chloride, diethylaluminum chloride and diethylmonoethoxyaluminum, a modified organoaluminum compound having Al-O-Al bonds, or a silane compound.

The inorganic carrier may be used after treatment with an active hydrogen-containing compound such as alcohol and aldehydes, an electron-donative compound such as ester and ether, or an alkoxide-containing compound such as tetraalkoxysilicate, trialkoxyaluminum and transition-metal tetraalkoxide.

The carriers may be contacted with various pretreating compounds in an atmosphere of an inert gas such as nitrogen or argon in the presence of an inert liquid hydrocarbon such as an aromatic hydrocarbon (6-12 carbon atoms) including benzene, toluene, xylene and ethylbenzene or an aliphatic or alicyclic hydrocarbon (5 - 12 carbon atoms) including heptane, hexane, decane, dodecane and cyclohexane, with or without stirring at -100° - 200°C, preferably -50° - 100°C for 30 minutes to 50 hours, preferably 1 - 24 hours. This pretreatment reaction is carried out preferably in the presence of a solvent of aromatic hydrocarbon such as benzene, toluene, xylene and ethylbenzene in which the

pretreating compounds are rendered soluble. The resulting carrier may be readily put to use for the preparation of catalyst components without having to remove the solvent. If the pretreating compound, for example a modified organoaluminum compound, is insoluble or hardly soluble, there may be added pentene, hexane, decane, dodecane or cyclohexane to allow the reaction product to precipitate and thereafter dry. Alternatively, part or all of the aromatic hydrocarbon solvent may be removed as by means of drying.

There is no particular restriction imposed upon the ratio of carrier/pretreating compound, the latter being usually 1 - 10,000 millimoles, preferably 5 - 1,500 millimoles per 100 grams carrier.

The various components (i) - (iv) used in the invention may be contacted in the following order:

- (1) Components (i) through (iv) are all simultaneously contacted together.
- (2) Components (i), (ii) and (iii) are contacted together and thereafter with component (iv).
- (3) Components (ii), (iii) and (iv) are contacted together and thereafter with component (i).
- (4) Components (i), (iii) and (iv) are contacted together and thereafter with component (ii).
- (5) Components (i), (ii) and (iv) are contacted together and thereafter with component (iii).
- (6) Components (i) and (ii) are contacted together, then with component (iii) and thereafter with component (iv).
- (7) Components (i) and (ii) are contacted together, then with component (iv) and thereafter with component (iii).
- (8) Components (i) and (iii) are contacted together, then with component (iv) and thereafter with component (ii).
- (9) Components (i) and (iii) are contacted together, then with component (iv) and thereafter with component (ii).
- (10) Components (i) and (iv) are contacted together, then with component (ii) and thereafter with component (iii).
- (11) Components (i) and (iv) are contacted together, then with component (iii) and thereafter with component (ii).
- (12) Components (ii) and (iii) are contacted together, then with component (i) and thereafter with component (iv).
- (13) Components (ii) and (iii) are contacted together, then with component (iv) and thereafter with component (i).
- (14) Components (ii) and (iv) are contacted together, then with component (i) and thereafter with component (iii).
- (15) Components (ii) and (iv) are contacted together, then with component (iii) and thereafter with component (i).
- (16) Components (iii) and (iv) are contacted together, then with component (i) and thereafter with component (ii).
- (17) Components (iii) and (iv) are contacted together, then with component (ii) and thereafter with component (i).
- (18) Components (i) and (iv) are contacted together, then with component (ii) and thereafter with component (iii).
- (19) Components (i) and (iv) are contacted together, then with component (iii) and thereafter with component (ii).

It has now been found that the sequences (1), (2), (5), (7) and (8) above are most effective.

These four components (i) through (iv) may be, not restrictively, contacted in an atmosphere of an inert gas such as nitrogen or argon in the presence of an inert liquid hydrocarbon such as an aromatic hydrocarbon (6 - 12 carbon atoms) including benzene, toluene, xylene and ethylbenzene, or an aliphatic or alicyclic hydrocarbon (5 - 12 carbon atoms) including heptane, hexane, decane, dodecane and cyclohexane, with or without stirring at -100° - 200°C, preferably -50° - 100°C for 30 minutes to 50 hours, preferably 1 - 24 hours. It is to be noted however that the reaction is conducted under conditions to retain the polymer carrier material substantially in a solid state.

Amongst the listed solvents are used most advantageously the aromatic hydrocarbons because the components (i), (ii) and (iii) are all soluble therein. Reference is made to the earlier mentioned procedures of pretreating the carrier materials for the utilization or disposal of the inert hydrocarbon solvents commonly used.

Component (ii) is used in an amount of 0.01 - 1,000 moles, preferably 0.1 - 100 moles, more preferably 1 - 10 moles per mole of component (i). Component (iii) is used in an amount of 0.01 - 100 moles, preferably 0.1 - 10 moles, more preferably 1 - 5 moles per mole of component (i). Component (i) is used in an amount by transition-metal concentration (Me) of 0.01 - 500 millimoles, preferably 0.05 - 200 millimoles, more preferably 0.1 - 20 millimoles per 100 g of carrier (iv). The catalyst components used in the invention should have an atomic ratio of Al/Me<sup>1</sup> in the range of 0.1 - 2,000, preferably 15 - 1,000.

The term modified organoaluminum compound (II) is used herein to designate a reaction product of an organoaluminum compound and water which has 1 - 100, preferably 1 - 50 Al-O-Al bonds in the molecule. This reaction is usually conducted in the presence of an inert hydrocarbon such as pentane, hexane, heptane, cyclohexane, methylcyclohexane, benzene, toluene and xylene, of which aliphatic and aromatic hydrocarbons are preferred. The starting organoaluminum compound may be represented by the formula



where R is an alkyl, alkenyl, aryl or aralkyl group having a carbon number of 1 - 24, preferably 1 - 12; X is a halogen atom; and n is an integer of 0 < n ≤ 3.

The above compound is typically exemplified by trialkylaluminum having an alkyl group optionally such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, hexyl, octyl, decyl and dodecyl groups, of which methyl group is particularly preferred.

The water/organoaluminum reaction takes place in a molar ratio of water:Al in the range of 0.25:1-1.2/1, preferably 0.5:1-1/1 at a temperature of usually -70° - 100°C, preferably -20° - 20°C for a period of 5 - 24 hours, preferably 5 - 10 hours. As water for reaction with the organoaluminum compound, there may be used crystal water contained in hydrates of copper sulfate or aluminum sulfate.

5 The catalyst component (I) and the modified organoaluminum compound (II) may be supplied separately or as an admixture to the polymerization reaction system. In either case, they are used in a ratio such that the atomic ratio of aluminum in the organoaluminum compound (II) to transition metal in the catalyst component (I) remain in the range of 1 - 100,000, preferably 5 - 1,000.

The term olefins as used herein designates alpha-olefins, cyclic olefins, dienes, trienes and styrene analogs. 10 Alpha-olefins have a carbon number of 2 - 12, preferably 2 - 8 and typically include ethylene, propylene, butene-1, hexene-1 and 4-methylpentene-1. These olefins may be homopolymerized or copolymerized such as by alternating, random or block copolymerization process.

The inventive process may be effectively applied where a diene compound such as butadiene, 1,4-hexadiene, ethylidene norbornene and dicyclopentadiene is used to reform the polymer product. In such a copolymerization reaction for example of ethylene and an alpha-olefin of 3 - 12 carbon atoms, it is desirable to hold an alpha-olefin content in the ethylene/alpha-olefin copolymer to 40 mole % or less, preferably 30 mole % or less, more preferably 20 mole % or less.

The polymerization reaction according to the invention is conducted in a slurry, solution or gas phase in the presence or absence of an inert hydrocarbon solvent such as an aliphatic hydrocarbon including hexane and heptane, an aromatic hydrocarbon including benzene, toluene and xylene, and an alicyclic hydrocarbon including cyclohexane, and methylcyclohexane, substantially without the presence of oxygen and water, at a temperature of 20° - 200°C, preferably 50° - 100°C under a pressure of atmospheric - 70 kg/cm<sup>2</sup>G, preferably atmospheric - 20 kg/cm<sup>2</sup>G, for a time length of 5 minutes to 10 hours, preferably 5 minutes to 5 hours.

Whilst the molecular weight of the polymer product obtained may be adjusted to some extent by varying the polymerization temperature, the molar ratio off the catalyst and other polymerization parameters, it can be more effectively adjusted by introducing hydrogen into the reaction system.

The inventive process can be advantageously used also in multi-stage polymerizations where hydrogen concentration and reaction temperature vary.

The invention will be further described by way of the following examples.

#### 30 Preparation of Modified Organoaluminum Compound (Methylalumoxane)

A 300-ml three-necked flask equipped with an electromagnetic stirrer was charged with 13 grams of copper sulfate heptahydrate and 50 ml of toluene. The admixture after being suspended was added at 0°C and over 2 hours with drops of 150 ml of a 1 mmol/ml triethylaluminum solution. The reaction was effected at 25°C for 24 hours. Filtration of the reaction mixture and subsequent evaporation of excess toluene gave 4 grams of methylalumoxane (MAO) in the form of a white crystal.

#### 40 Preparation of Catalyst Component A

##### (1) Pretreatment of Carrier (iv)

A 300 cc three-necked flask was charged with 100 ml refined toluene and 10 g SiO<sub>2</sub> (surface area 300 m<sup>2</sup>/g, Grade No. 952 of Fuji Davison) which had been calcined at 460°C for 5 hours in nitrogen atmosphere, followed by addition of 45 6 ml toluene solution of methylalumoxane (concentration 2.5 mmol/ml). The admixture was stirred at room temperature for 2 hours and thereafter dried by nitrogen blow to yield a fluid particulate product.

##### (2) Preparation of Transition Metal Catalyst Component [Components (i)+(ii)+(iii)]

50 A 300 cc three-necked flask was charged with 100 ml refined toluene, 50 ml tetrahydrofuran (THF) solution of ethylmagnesium chloride (EtMgCl) (concentration 2 mols/l) and 2.2 g indene and cooled at -60°C. A separate flask was charged with 50 ml toluene, 4.2 g tetrapropoxyzirconium (Zr(OPr)<sub>4</sub>) and 0.8 g indene. This solution was fed into the first flask, and the whole mixture therein was stirred at -60°C for 1 hour, followed by heating with continued stirring up to 20°C slowly over 2 hours. The reaction was continued at 45°C for 3 hours.

##### 55 (3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

A 300 cc three-necked flask was charged with 10 g carrier prepared as above in nitrogen atmosphere and 30 ml

toluene solution of transition metal catalyst component prepared as above, followed by 15 ml refined toluene. The admixture was stirred at room temperature for 2 hours, followed by removal of the solvent by nitrogen blow in vacuum thereby obtaining 11 g solid catalyst component A.

#### 5 Preparation of Catalyst Component B

##### (1) Pretreatment of Carrier (iv)

The same as for catalyst component A.

10

##### (2) Preparation of Transition Metal Catalyst Component [Components (i)+(ii)+(iii)]

A 300 cc three-necked flask was charged with 100 ml refined toluene, 9.8 g triethylboron ( $\text{Et}_3\text{B}$ ) and 2.5 g cyclopentadiene and cooled at  $-60^\circ\text{C}$ . A separate flask was charged with 4.2 g tetrapropoxyzirconium and 0.84  
15 cyclopentadiene. The rest of the procedure was the same as in the preparation of Component A.

##### (3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

A 300 cc three-necked flask was charged with 10 g carrier prepared as above in nitrogen atmosphere and 35 ml  
20 toluene solution of transition metal catalyst component prepared as above, followed by addition of 15 ml refined toluene. The admixture was stirred at room temperature for 2 hours, followed by removal of the solvent by nitrogen blow in vacuum thereby obtaining solid catalyst component B.

#### Preparation of Catalyst Component C

25

##### (1) Carrier (iv)

10 g  $\text{SiO}_2$  (surface area  $300 \text{ m}^2/\text{g}$ , Grade No. 952 of Fuji Davison) was used, which had been calcined at  $600^\circ\text{C}$  for 5 hours. This carrier was not pretreated.

30

##### (2) Preparation of Transition Metal Catalyst Component [Components (i)+(ii)+(iii)]

A 300 cc three-necked flask was charged with 100 ml refined toluene, 25 ml tetrahydrofuran solution of n-butylmagnesium chloride (concentration 2 mols/l) and 1.7 g cyclopentadiene and stirred at room temperature for 30 minutes, followed by addition over 20 minutes of 4.2 g tetrapropoxyzirconium dissolved in 50 ml toluene. The reaction was  
35 continued at  $45^\circ\text{C}$  for 3 hours.

##### (3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

A 300 cc three-necked flask was charged with 10 g carrier prepared as above in nitrogen atmosphere and 29 ml  
40 toluene solution of transition metal catalyst component prepared as above, followed by addition of 15 ml refined toluene. The admixture was stirred at room temperature for 2 hours, followed by removal of the solvent by nitrogen blow in vacuum thereby obtaining solid catalyst component C.

#### 45 Preparation of Catalyst Component D

##### (1) Pretreatment of Carrier (iv)

A 400 ml stainless steel pot containing 25 pieces of half inch stainless steel balls was charged with 10 g magnesium anhydrous chloride and 3.8 g triethoxyaluminum. The admixture was subjected to ball-milling in nitrogen atmosphere at room temperature.

50

##### (2) Preparation of Transition Metal Catalyst Component [Components (i)+(ii)+(iii)]

A 300 cc three-necked flask was charged with 100 ml refined toluene, 15.7 g of diethylzinc ( $\text{Et}_2\text{Zn}$ ) and 5.9 g indene and stirred at room temperature for 30 minutes. 4.2 g tetrapropoxyzirconium dissolved in 50 ml toluene was added over 20 minutes. The reaction was continued at  $45^\circ\text{C}$  for 3 hours.

55

## (3) Preparation of Solid Catalyst Component [(i)+(ii)+(iii)+(iv)]

A 300 cc three-necked flask was charged with 10 g carrier prepared as above in nitrogen atmosphere and 27 ml toluene solution of transition metal catalyst component prepared as above, followed by addition of 15 ml refined toluene. The admixture was stirred at room temperature for 2 hours, followed by removal of the solvent by nitrogen blow in vacuum thereby obtaining solid catalyst component D.

Preparation of Catalyst Component E

## (1) Pretreatment of Carrier (iv)

10 g polyethylene powder dried at 60°C for 3 hours (MFR 1.0 g/10 min, bulk density 0.41 g/cc, particle size 500 µm, melting point 121°C) was added dispersively with 6 ml toluene solution of methylalumoxane (concentration 2.5 mmol/ml). The admixture was stirred at room temperature for 1 hour, followed by drying with nitrogen blow thereby obtaining a fluid particulate product.

## (2) Preparation of Transition Metal Catalyst Component [(i)+(ii)+(iii)]

The procedure for the preparation of Catalyst Component A was followed except that 64 ml tetrahydrofuran solution of ethylmagnesium bromide (EtMgBr) (concentration 2 mols/l).

## (3) Preparation of Solid Catalyst Component [(i)+(ii)+(iii)+(iv)]

A 300 cc three-necked flask was charged with 10 g carrier prepared as above in nitrogen atmosphere and 38 ml toluene solution of transition metal catalyst component prepared as above, followed by addition of 15 ml refined toluene. The admixture was stirred at room temperature for 2 hours, followed by removal of the solvent by nitrogen blow in vacuum thereby obtaining solid catalyst component E.

Preparation of Catalyst Component F

## (1) Pretreatment of Carrier (iv)

The procedure for the preparation of Catalyst Component A was followed except that 10 g Al<sub>2</sub>O<sub>3</sub> (surface area 300 m<sup>2</sup>/g and average particle size 60 µm) was used, which had been calcined at 400°C for 5 hours.

## (2) Preparation of Transition Metal Catalyst Component [(i)+(ii)+(iii)]

A 300 cc three-necked flask was charged with 100 ml refined toluene, 64 ml THF solution of ethylmagnesium chloride (concentration 2 mols/l) and 4.0 g methylcyclopentadiene. The admixture was stirred at room temperature for 30 minutes, followed by addition over 20 minutes of 4.9 g tetrabutoxyzirconium (Zr(OnBt)<sub>4</sub>) dissolved in 50 ml toluene. The reaction was continued with stirring at 45°C for 3 hours.

## (3) Preparation of Solid Catalyst Component [(i)+(ii)+(iii)+(iv)]

The procedure for Catalyst Component A was followed except that the above solution of transition metal component was mixed with the carrier (iv) such that Zr deposits were 2.1 wt%.

Preparation of Catalyst Component G

## (1) Pretreatment of Carrier (iv)

The procedure for the preparation of Catalyst Component A was followed except that 15 ml n-hexane solution of trimethylaluminum (AlMe<sub>3</sub>) (concentration 1 mmol/ml) was used.

## (2) Preparation of Transition Metal Catalyst Component [(i)+(ii)+(iii)]

A 300 cc three-necked flask was charged with 100 ml refined toluene, 64 ml THF solution of ethylmagnesium chloride (2 mols/l) and 3.4 cyclopentadiene. The admixture was stirred at room temperature for 30 minutes, followed by

addition over 20 minutes of 3.9 g tripropoxychlorozirconium ( $\text{Zr}(\text{OPr})_3\text{Cl}$ ) dissolved in 50 ml toluene. The reaction was continued with stirring at 45°C for 3 hours.

(3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

The procedure for Catalyst Component A was followed except that the above solution of transition metal component was mixed with the carrier (iv) such that the amount of Zr deposits was 2 wt%.

Preparation of Catalyst Component H

(1) Pretreatment of Carrier (iv)

The same as for Catalyst Component A.

(2) Preparation of Transition Metal Catalyst Component [Components (i)+(ii)+(iii)]

A 300 cc three-necked flask was charged with 100 ml refined toluene, 26 ml THF solution of ethylmagnesium chloride (concentration 2 mol/l) and 6.6 g bisindenylethane. The admixture was stirred at room temperature for 30 minutes, followed by addition over 20 minutes of 3.5 g tetraethoxyzirconium ( $\text{Zr}(\text{OEt})_4$ ) dissolved in 50 ml toluene. The reaction was continued with stirring at 45°C for 3 hours.

(3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

The procedure for Catalyst Component A was followed except that the above solution of transition metal component was mixed with the above carrier (iv) such that Zr deposits were 1.9 wt%.

Preparation of Catalyst Component I

(1) Pretreatment of Carrier (iv)

The same as for Catalyst Component A.

(2) Preparation of Transition Metal Catalyst Component [Components (i)+(ii)+(iii)]

The procedure for Catalyst Component H was followed except that 4.8 g biscyclopentadienyldimethyl silane was used.

(3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

The procedure for Catalyst Component A was followed except that the above solution of transition metal component was mixed with the above carrier (iv) such that Zr deposits were 1.9 wt%.

Preparation of Catalyst Component J - P

(1) Pretreatment of Carrier (iv)

The same as for Catalyst Component A.

(2) Preparation of Transition Metal Catalyst Component [Component (i)+(ii)+(iii)]

The transition metal catalyst components prepared are shown and identified in Table 1.

(3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

The procedure for Catalyst Component A was followed to obtain Catalyst Components J - P having respective metal deposits as shown in Table 1.

Preparation of Catalyst Component A'

## (1) Pretreatment of Carrier (iv)

- 5 A 300 cc three-necked flask was charged with 100 ml refined toluene and 10 g SiO<sub>2</sub> (surface area 300 m<sup>2</sup>/g, Grade No. 952 of Fuji Davison) which had been calcined at 460°C for 5 hours in nitrogen atmosphere, followed by addition of 6 ml toluene solution of methylalumoxane (concentration 2.5 mmol/ml). The admixture was stirred at room temperature for 2 hours and thereafter dried by nitrogen blow to yield a fluid particulate product.

## 10 (2) Preparation of Transition Metal Catalyst Component [Components (i)+(ii)+(iii)]

- A 300 cc three-necked flask was charged with 100 ml refined toluene, 5.84 g triethylaluminum (AlEt<sub>3</sub>) and 2.2 g indene and cooled at -60°C. A separate flask was charged with 50 ml toluene, 4.2 g tetrapropoxyzirconium (Zr(OPr)<sub>4</sub>) and 0.8 g indene. This solution was fed into the first flask, and the whole mixture therein was stirred at -60°C for 1 hour, followed by heating with continued stirring up to 20°C slowly over 2 hours. The reaction was continued at 45°C for 3 hours until there was obtained a black solution containing 0.075 mmol/ml Zr.

## (3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

- 20 A 300 cc three-necked flask was charged with 10 g carrier prepared as above in nitrogen atmosphere and 30 ml toluene solution of transition metal catalyst component prepared as above, followed by addition of 15 ml refined toluene. The admixture was stirred at room temperature for 2 hours, followed by removal of the solvent by nitrogen blow in vacuum thereby obtaining 11 g solid catalyst component A'.

25 Preparation of Catalyst Component B'

## (1) Pretreatment of Carrier (iv)

The same as for catalyst component A'.

30

## (2) Preparation of Transition Metal Catalyst Component [Components (i)+(ii)+(iii)]

- A 300 cc three-necked flask was charged with 100 ml refined toluene, 5.84 g triethylaluminum (AlEt<sub>3</sub>) and 0.60 g cyclopentadiene and cooled at -60°C. A separate flask was charged with 50 ml toluene, 4.2 g tetrapropoxyzirconium and 0.24 g cyclopentadiene. The rest of the procedure was the same as in the preparation of Component A'.

35

## (3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

The same as for Catalyst Component A'.

40

Preparation of Catalyst Component C'

## (1) Carrier (iv)

- 45 The same SiO<sub>2</sub> as in Catalyst Component A' was used. This carrier was not pretreated.

## (2) Preparation of Transition Metal Catalyst Component [Components (i)+(ii)+(iii)]

- A 300 cc three-necked flask was charged with 100 ml refined toluene, 13.3 g AlEt<sub>2</sub>(OEt) and 2.4 g cyclopentadiene and cooled at -60°C. A separate flask was charged with 50 ml toluene, 4.2 g Zr(OPr)<sub>4</sub> and 1.0 g cyclopentadiene. The rest of the procedure was the same as in the preparation of Component A'.

50

## (3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

- 55 The same as for Catalyst Component A'.

Preparation of Catalyst Component D'

## (1) Pretreatment of Carrier (iv)

5 In place of silica, there was used alumina  $\text{Al}_2\text{O}_3$  (surface area  $300 \text{ m}^2/\text{g}$  and average particle size  $60 \mu\text{m}$ ) which was pretreated as per Catalyst Component A'.

## (2) Preparation of Transition Metal Catalyst Component [Components (i)+(ii)+(iii)]

10 A 300 cc three-necked flask was charged with 100 ml refined toluene, 5.84 g triethylaluminum and 2.53 g methylcyclopentadiene and cooled at  $-60^\circ\text{C}$ . A separate flask was charged with 50 ml toluene, 4.93 g  $\text{Zr}(\text{OBu})_4$  and 1 g methylcyclopentadiene. The rest of the procedure was the same as in the preparation of Component A'.

## (3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

15

The same as for Catalyst Component A'.

Preparation of Catalyst Component E'

## 20 (1) Pretreatment of Carrier (iv)

A 400 ml stainless steel pot containing 25 pieces of half inch stainless steel balls was charge with 10 g magnesium anhydrous chloride and 3.8 g triethoxyaluminum. The admixture was subjected to ball-milling in nitrogen atmosphere at room temperature. 10 g milled product was used as the carrier.

25

## (2) Preparation of Transition Metal Catalyst Component [Components (i)+(ii)+(iii)]

The same as for Catalyst Component A'.

## 30 (3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

The same as for Catalyst Component A'.

Preparation of Catalyst Component F'

35

## (1) Pretreatment of Carrier (iv)

40 A 300 ml three-necked flask was charged with 100 ml refined toluene, 10 g polyethylene powder (MFR 1.0/10 min, density  $0.9210 \text{ g/cm}^3$ , bulk density  $0.41 \text{ g/cc}$ , particle size  $500 \mu\text{m}$  and melting point  $121^\circ\text{C}$ ) and 6 ml toluene solution of methylaluminoxane which was uniformly dispersed over the polyethylene powder in nitrogen atmosphere.

## (2) Preparation of Transition Metal Catalyst Component [Components (i)+(ii)+(iii)]

45 A 300 cc three-necked flask was charged with 100 ml refined toluene, 5.8 g triethylaluminum, 3g indene and 4.2 g  $\text{Zr}(\text{OPr})_4$  in nitrogen atmosphere at room temperature. The admixture was stirred at  $45^\circ\text{C}$  for 2 hours.

## (3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

The same as for Catalyst Component A'.

50

Preparation of Catalyst Component G'

## (1) Pretreatment of Carrier (iv)

55 The procedure for the preparation of Catalyst Component A' was followed except that silica - alumina (surface area  $300 \text{ m}^2/\text{g}$ , pore volume  $0.7 \text{ cc/g}$  and average particle size  $50 \mu\text{m}$ ) was used in place of silica.

## (2) Preparation of Transition Metal Catalyst Component [Components (i)+(ii)+(iii)]

A 300 cc three-necked flask was charged with 150 ml refined toluene, 15.4 g  $\text{AlEt}_2\text{Cl}$ , 4.2 g  $\text{Zr}(\text{OPr})_4$  and 3.4 g cyclopentadiene in nitrogen atmosphere at room temperature. The admixture was stirred at 45°C for 2 hours.

## (3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

The same as for Catalyst Component A'.

Preparation of Catalyst Component H'

## (1) Pretreatment of Carrier (iv)

The same as for Catalyst Component A'.

## (2) Preparation of Transition Metal Catalyst Component [Components (i)+(ii)+(iii)]

A 300 cc three-necked flask was charged with 50 ml refined toluene, 5.84 g triethylaluminum, 4.85 g biscyclopentadienyldimethylsilane, and 3.5 g  $\text{Zr}(\text{OEt})_4$  in nitrogen atmosphere at room temperature. The admixture was stirred at 45°C for 2 hours.

## (3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

The same as for Catalyst Component A'.

Preparation of Catalyst Component I'

## (1) Pretreatment of Carrier (iv)

The same as for Catalyst Component A'.

## (2) Preparation of Transition Metal Catalyst Component [Components (i)+(ii)+(iii)]

A 300 cc three-necked flask was charged with 150 ml refined toluene, 5.84 g triethylaluminum, 3.7 g biscyclopentadienylmethane and 4.2 g  $\text{Zr}(\text{OPr})_4$  in nitrogen atmosphere at room temperature. The admixture was stirred at 45°C for 2 hours.

## (3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

The same as for Catalyst Component A'.

Preparation of Catalyst Component J'

## (1) Pretreatment of Carrier (iv)

The procedure for Catalyst Component A' was followed except that 15 ml toluene solution of trimethylaluminum (concentration 1 mmol/ml) was used in place of methylalumoxane.

## (2) Preparation of Transition Metal Catalyst Component [Component (i)+(ii)+(iii)]

A 300 cc three necked flask was charged with 150 ml refined toluene, 11.7 g triethylaluminum, 13.4 g bisindenylethane and 3.9 g  $\text{Zr}(\text{OPr})_4\text{Cl}$  in nitrogen atmosphere at room temperature. The admixture was stirred at 45°C for 2 hours.

## (3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

The procedure for Catalyst Component A' was followed.

Preparation of Catalyst Component K'

## (1) Pretreatment of Carrier (iv)

5 The same as for catalyst component A'.

## (2) Preparation of Transition Metal Catalyst Component [Components (i)+(ii)+(iii)]

10 3 g zirconium tetrachloride was admixed with an ether solution of magnesium benzylchloride and let alone at -20°C for 2 hours, followed by stirring at room temperature for 2 hours. Byproduced  $MgCl_2$  was removed, and the ether solution was concentrated and cooled to -20°C until there was obtained a crystalline product ( $ZrBz_4$ ) having a melting point of 112.8°C.

A 300 cc three-necked flask was charged with 150 ml refined toluene, 14.6 g triethylaluminum, 2.54 g cyclopentadiene and 5.8 g  $ZrBz_4$ . The admixture was stirred at 45°C for 2 hours.

15 (3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

The same as for Catalyst Component A'.

20 Preparation of Catalyst Component L'

## (1) Pretreatment of Carrier (iv)

The same as for catalyst component A'.

25

## (2) Preparation of Transition Metal Catalyst Component [Components (i)+(ii)+(iii)]

The procedure for Catalyst Component K' was followed except that titanium tetrachloride was used in place of zirconium tetrachloride to produce  $TiBz_4$ .

30 A 300 cc three-necked flask was charged with 150 ml refined toluene, 14.6 g triethylaluminum, 5.2 g pentamethylcyclopentadiene and 5.3 g  $TiBz_4$  in nitrogen atmosphere. The admixture was stirred at 45°C for 2 hours.

## (3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

35 The same as for Catalyst Component A'.

Preparation of Catalyst Component M'

## (1) Pretreatment of Carrier (iv)

40

The same as for catalyst component A'.

## (2) Preparation of Transition Metal Catalyst Component [Components (i)+(ii)+(iii)]

45 The procedure for Catalyst Component K' was followed except that hafnium tetrachloride was used in place of  $ZrBz_4$  to produce  $HfBz_4$ .

A 300 cc three-necked flask was charged with 150 ml refined toluene, 14.6 g triethylaluminum, 2.54 g cyclopentadiene and 5.8 g  $ZrBz_4$ . The admixture was stirred at 45°C for 2 hours.

50 (3) Preparation of Solid Catalyst Component [Components (i)+(ii)+(iii)+(iv)]

The same as for Catalyst Component A'.

Preparation of Catalyst Component N'

55

## (1) Pretreatment of Carrier (iv)

The procedure for Catalyst Component A' was followed except that 15 ml hexane solution of  $Zr(OPr)_4$  (concentra-

tion 1 mmol/ml) was used in place of methylaloxane.

(2) Preparation of Solid Catalyst Component [(i)+(ii)+(iii)+(iv)]

5 A 300 cc three-necked flask was charged with 10 g carrier prepared as above, 100 ml refined n-hexane, 0.84 g tri-ethylaluminum and 0.12 g cyclopentadiene. The admixture was stirred at room temperature for 2 hours, followed by addition of 0.5 g  $\text{Zr}(\text{OEt})_4$ , and thereafter stirred at 45°C for 2 hours in nitrogen atmosphere. The solvent was removed by nitrogen blow in vacuum.

10 Preparation of Catalyst Component O'

(1) Pretreatment of Carrier (iv)

The procedure for Catalyst Component A' was followed except that 10 g  $\text{Mg}(\text{CO}_3)_2$  powder dried at 150°C for 2  
15 hours was used in place of silica.

(2) Preparation of Transition Metal Catalyst

The same as for Catalyst Component A'.

20

(3) Preparation of Solid Catalyst Component [(i)+(ii)+(iii)+(iv)]

The same as for Catalyst Component A'.

25 Inventive Example 1

A 3-liter stainless steel autoclave equipped with stirrer was purged with nitrogen and thereafter supplied with 200 g of dry salt, 22 ml of 1 mmol/ml methylaloxane solution and 100 mg of Catalyst Component A. The admixture was heated at 60°C with stirring. A mix of ethylene and butene-1 gases (butene-1/ethylene molar ratio 0.25) was charged to  
30 bring the reactor pressure up to 9 kgf/cm<sup>2</sup>G, whereupon polymerization reaction was initiated and continued for 1 hour with continued charge of a mixed gas of ethylene and butene-1 (butene-1/ethylene molar ratio 0.05) to maintain the reaction system at 9 kgf/cm<sup>2</sup>G.

Upon completion of the reaction, excess gas was removed from the reactor which was then cooled to yield 66 grams of a white polymer.

35

Inventive Examples 2 - 16

The procedure of Inventive Example 1 was followed for the polymerization under the conditions shown in Table 1 and with the results shown in Table 2.

40

Inventive Example 17

The procedure of Inventive Example 1 was followed for homopolymerization of ethylene under the conditions indicated in Table 1 and with the results shown in Table 2, except that an ethylene gas was used for pressure control in  
45 place of a mixed gas of ethylene and butene-1.

Inventive Example 18

The procedure of Inventive Example 1 was followed except that propylene gas was used in the homopolymerization of propylene and that the reaction temperature and pressure were 50°C and 7 kgf/cm<sup>2</sup>G, respectively.

50

Comparative Example 1 - 3

The procedure of Inventive Example 1 was followed under the conditions shown in Table 1 and with the results in  
55 Table 2.

## Inventive Example 19

A 3-liter stainless steel autoclave equipped with stirrer was purged with nitrogen and thereafter supplied with 200 g of dry salt, 22 ml of 1 mmol/ml methylalumoxane solution and 100 mg of Catalyst Component A'. The admixture was heated at 60°C with stirring. A mix of ethylene and butene-1 gases (butene-1/ethylene molar ratio 0.25) was charged to bring the reactor pressure up to 9 kgf/cm<sup>2</sup>G, whereupon polymerization reaction was initiated and continued for 1 hour with continued charge of a mixed gas of ethylene and butene-1 (butene-1/ethylene molar ratio 0.05) to maintain the reaction system at 9 kgf/cm<sup>2</sup>G.

Upon completion of the reaction, excess gas was removed from the reactor which was then cooled to yield 76 grams of a white polymer.

Table 2 shows the polymerization results and the properties of resultant polymers (Inventive Examples 1 - 18 and Comparative Examples 1 - 3).

## Inventive Examples 20 - 35

The procedure of Inventive Example 19 was followed that Catalyst Components B' - O' were used in place of Catalyst Component A' as indicated in Table 3.

## Comparative Examples 4 - 6

The procedure of Inventive Example 19 was followed except that Catalyst Components T, U and V were used in place of Catalyst Component A'.

Table 4 shows the polymerization results and the properties of resultant polymers (Inventive Examples 19 - 35 and Comparative Examples 4 - 6).

Each of the polymers obtained in the respective Inventive and Comparative Examples was subjected to the following tests.

Melt Index (MI)

The procedure of ASTM D1238-57T was followed.

Density (D)

The procedure of ASTM D1505-68 was followed.

Melting Point by Calorimetry (DSC)

5 mg of the polymer sample was disposed at 180°C for 3 minutes, cooled to 0°C over 10°C/min and allowed to stand at 0°C for 10 minutes, followed by heating with a temperature rise of 10°C/min with use of a melting point tester (Seiko Electronics DSC-20).

Table 1

	Catalyst lot	solid catalyst component				composition ratio (i):(ii):(iii): mol ratio	transition metal deposits wt%	amount of addition during polymerization transition metal mg	Al/Me ratio
		carrier (iv)	component (i)	component (iii)	component (ii)				
1	A	SiO <sub>2</sub> -MAO	Zr(OPr) <sub>4</sub>	indene	EtMgCl	1 : 4 : 8	2	1.9	MAO
2	B	"	"	cyclopentadiene	Et <sub>3</sub> B	"	"	2.0	"
3	C	SiO <sub>2</sub>	"	"	nBuMgCl	1 : 2 : 4	1.9	1.8	"
4	D	MgCl <sub>2</sub> -Al(OEt) <sub>3</sub>	"	indene	Et <sub>2</sub> Zn	1 : 4 : 10	1.8	1.7	"
5	E	PE polymer-MAO	"	"	EtMgBr	"	2.0	1.9	"
6	F	Al <sub>2</sub> O <sub>3</sub>	Zr(O <sup>n</sup> Bu) <sub>4</sub>	methylcyclopentadiene	"	"	"	2.1	"
7	G	SiO <sub>2</sub> -AlMe <sub>3</sub>	Zr(OPr) <sub>3</sub> Cl	cyclopentadiene	EtMgCl	"	"	1.7	"
8	H	SiO <sub>2</sub> -MAO	Zr(OEt) <sub>4</sub>	bis-indenyl-ethane	"	1 : 2 : 4	1.9	1.8	"
9	I	"	"	bis-cyclopentadienyl-dimethyl silane	"	"	"	1.9	"
10	J	"	"	bis-cyclopentadienyl methane	"	"	"	1.8	"

Table 1 (cont'd)

	Catalyst lot	solid catalyst component				composition ratio (i):(ii):(iii): mol ratio	transition metal deposits wt%	amount of addition during polymerization		Al/Me ratio
		carrier (iv)	component (i)	component (iii)	component (ii)			transition metal mg	modified Al	
IE 11	K	SiO <sub>2</sub> -MAO	Ti(OnBu) <sub>3</sub> Cl	cyclopentadiene	EtMgCl	1 : 3 : 10	2.0	2.3	MAO	1000
12	L	"	ZrBz <sub>4</sub>	"	"	1 : 4 : 8	"	1.9	"	"
13	M	"	Zr(neophil) <sub>4</sub>	pentamethylcyclopentadiene	"	"	"	1.7	"	"
14	N	"	ZrCl <sub>4</sub>	cyclopentadiene	EtLi	1 : 2 : 6	"	2.1	"	"
15	O	"	TiCl <sub>4</sub>	"	EtMgCl	1 : 2 : 4	"	2.0	"	"
16	P	"	Hf(OPr) <sub>4</sub>	"	"	1 : 4 : 8	"	2.4	"	"
17	H	"	Zr(OEt) <sub>4</sub>	bis-indenyl-ethane	"	1 : 2 : 4	1.9	1.8	"	"
18	H	"	"	"	"	"	"	"	"	"
CE 1	Q	-	Zr(OPr) <sub>4</sub>	indene	EtMgCl	1 : 4 : 8	-	1.7	"	"
2	R	SiO <sub>2</sub> -MAO	"	-	"	1 : 0 : 7	2	1.6	"	"
3	S	"	"	indene	-	1 : 4 : 0	"	1.5	"	"

IE : Inventive Example      CE : Comparative Example

Table 2

		yield g	catalytic activity g/gMe	MFR g/10 min	bulk density g/cc	polymer density g/cm <sup>3</sup>	melting point °C
5	IE 1	66	35,000	0.8	0.39	0.9210	114.0
	2	102	51,000	4.8	0.40	0.9215	104.7
10	3	82	46,000	5.1	0.38	0.9220	106.8
	4	62	37,000	0.6	0.35	0.9119	113.0
	5	74	39,000	0.4	0.33	0.9117	112.8
	6	90	43,000	2.1	0.41	0.9213	104.1
15	7	97	57,000	3.8	0.37	0.9225	106.3
	8	90	50,000	1.1	0.42	0.9218	108.7
	9	74	39,000	3.9	0.38	0.9119	103.8
20	10	52	29,000	2.5	0.39	0.9220	103.1
	11	53	23,000	3.7	0.36	0.9208	104.1
	12	59	31,000	8.4	0.35	0.9116	101.1
	13	70	41,000	7.9	0.38	0.9218	107.3
25	14	69	33,000	12.2	0.39	0.9231	108.0
	15	56	28,000	4.7	0.39	0.9222	106.9
	16	50	21,000	3.2	0.34	0.9210	103.9
30	17	106	59,000	2.8	0.41	0.9508	135.1
	18	56	31,000	2.0	0.37	0.9021	138.9
	CE 1	114	67,000	0.8	0.24	0.9196	113.0
	2	0	0	-	-	-	-
35	3	17	11,000	1.3	0.40	0.9280	115.8

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Table 3

	Catalyst lot	solid catalyst component					composition ratio (i):(ii):(iii) mol ratio	transi- tion metal deposits wt%	amount of addition during polymerization		Al/Me ratio
		carrier (iv)	component (i)	component (iii)	component (ii)	metal mg			modified Al		
IE 19	A'	SiO <sub>2</sub> -MAO	Zr(OPr) <sub>4</sub>	indene	AlEt <sub>3</sub>	1 : 2 : 4	2	2	MAO	1000	
20	B'	"	"	cyclopentadiene	"	"	1.5	"	"	"	
21	C'	SiO <sub>2</sub>	"	"	AlEt <sub>2</sub> (OEt)	1 : 4 : 8	"	1.8	"	"	
22	D'	Al <sub>2</sub> O <sub>3</sub> -MAO	Zr(OBu) <sub>4</sub>	methylcyclo- pentadiene	AlEt <sub>3</sub>	1 : 2 : 4	1.8	1.7	"	"	
23	E'	MgCl <sub>2</sub> -Al(OEt) <sub>3</sub>	Zr(OPr) <sub>4</sub>	indene	"	"	2.0	1.8	"	"	
24	F'	PE polymer-MAO	"	"	"	"	"	1.9	"	"	
25	G'	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -MAO	"	cyclopentadiene	AlEt <sub>2</sub> Cl	1 : 4 : 10	"	1.7	"	"	
26	H'	SiO <sub>2</sub> -MAO	Zr(OEt) <sub>4</sub>	bis-cyclo- pentadienyl- dimethyl silane	AlEt <sub>3</sub>	1 : 2 : 4	"	1.6	"	"	
27	I'	"	Zr(OPr) <sub>4</sub>	bis-cyclo- pentadienyl- methane	"	"	"	1.9	"	"	
28	J'	SiO <sub>2</sub> -AlMe <sub>3</sub>	Zr(OPr) <sub>3</sub> Cl	bis-indenyl- ethane	"	1 : 4 : 8	"	1.8	"	"	

Table 3 (cont'd)

	Catalyst lot	solid catalyst component				composition ratio (i):(ii):(iii) mol ratio	transition metal deposits wt%	amount of addition during polymerization transition metal mg	Al/Me ratio
		carrier (iv)	component (i)	component (iii)	component (ii)				
IE 29	K'	SiO <sub>2</sub> -MAO	ZrBz <sub>4</sub>	cyclopentadiene	AlEt <sub>3</sub>	1 : 3 : 10	1.9	1.7	MAO
30	L'	"	TiBz <sub>2</sub>	pentamethylcyclopentadiene	"	"	2.0	1.9	"
31	M'	"	HfBz <sub>4</sub>	cyclopentadiene	"	"	1.8	2.5	"
32	J'	SiO <sub>2</sub> -AlMe <sub>3</sub>	Zr(OPr) <sub>3</sub> Cl	bis-indenyl-ethane	"	1 : 4 : 8	2.0	1.6	"
33	J'	"	"	"	"	"	2.0	2.7	"
34	N'	SiO <sub>2</sub> -Zr(OPr) <sub>4</sub>	Zr(OEt) <sub>4</sub>	cyclopentadiene	"	1 : 2 : 4	10.0	1.8	"
35	O'	MKG(CO) <sub>3</sub> γ-MAO	Zr(OPr) <sub>4</sub>	indene	"	"	2.0	1.9	"
CE 4	T	-	Zr(OPr) <sub>4</sub>	indene	AlEt <sub>3</sub>	1 : 2 : 4	-	1.7	"
5	U	SiO <sub>2</sub> -MAO	"	-	"	1 : 0 : 4	2	1.6	"
6	V	"	"	indene	"	1 : 2 : 0	"	1.5	"

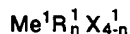
IE : Inventive Example    CE : Comparative Example

Table 4

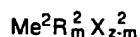
		yield g	catalytic activity g/gMe	MFR g/10 min	bulk density g/cc	polymer density g/cm3	melting point °C
5	IE 19	76	38,000	0.9	0.38	0.9221	114.1
	20	98	49,000	3.8	0.40	0.9215	104.5
10	21	57	32,000	4.3	0.41	0.9228	105.1
	22	73	43,000	2.8	0.39	0.9233	106.3
	23	67	37,000	0.7	0.30	0.9218	113.8
	24	76	40,000	0.8	0.33	0.9233	114.5
15	25	86	51,000	3.5	0.40	0.9235	106.5
	26	61	38,000	2.3	0.41	0.9229	105.3
	27	44	23,000	4.5	0.38	0.9217	104.8
20	28	95	53,000	0.9	0.40	0.9215	107.3
	29	73	43,000	6.2	0.36	0.9217	105.1
	30	66	35,000	1.1	0.35	0.9234	98.0
	31	72	29,000	2.9	0.39	0.9236	106.4
25	32	97	61,000	1.5	0.42	0.9510	135.1
	33	99	37,000	1.9	0.37	0.9054	139.7
	34	94	52,000	8.0	0.37	0.9218	105.7
30	35	47	25,000	0.1	0.31	0.9219	113.9
	CE 4	95	56,000	0.08	0.20	0.9196	113.0
	5	0	0	-	-	-	-
	6	17	11,000	1.3	0.40	0.9280	115.8
35	IE : Inventive Example CE : Comparative Example						

## Claims

1. A process for the manufacture of polyolefins which comprises polymerizing an olefinic hydrocarbon selected from the group consisting of alpha-olefins, cyclic olefins, dienes, trienes and styrene analogs in the presence of a catalyst composition, said catalyst composition comprising a first component (I) and a second component (II),  
said first component (I) resulting from the reaction of  
a compound (i) of the formula



wherein R<sup>1</sup> is an alkyl, alkoxy, aryloxy or aralkyloxy group of 1 - 24 carbon atoms, X<sup>1</sup> is a halogen atom, Me<sup>1</sup> is a metal of the group of zirconium, titanium and hafnium, and n is an integer of 0 ≤ n ≤ 4, in an amount by transition metal concentration of 0.01-500 millimoles per 100g of a carrier (iv) defined hereinafter;  
a compound (ii) of the formula



wherein R<sup>2</sup> is a hydrocarbon group of 1 - 24 carbon atoms, X<sup>2</sup> is an alkoxy group of 1 - 12 carbon atoms or a halogen atom, Me<sup>2</sup> is an element of Groups I-III in the Periodic Table, z is the valence of Me<sup>2</sup>, and m is an integer of 0 < m ≤ Z, in an amount of 0.01-100 moles per mole of said compound (i);  
an organocyclic compound (iii) in an amount of 0.01-10 moles per mole of said compound (i), said organo-

cyclic compound being selected from the group consisting of cyclic hydrocarbons having 2 or more conjugated double bonds in the molecule and a carbon number of 4-24; a compound of the formula



wherein Cp is a cyclopentadienyl group,  $R^3$  is a hydrocarbon group of 1-24 carbon atoms,  $X^3$  is a halogen atom, and r and s are  $0 < r \leq 4$  and  $0 \leq s \leq 3$  respectively, and a compound of the formula



wherein Ind is an indenyl group,  $R^4$  is a hydrocarbon group of 1-24 carbon atoms,  $X^4$  is a halogen atom; and t and u are  $0 < t \leq 4$  and  $0 \leq u \leq 3$  respectively; and

an inorganic carrier and/or particulate polymer carrier (iv);

said second component (II) being a modified organoaluminum compound having Al-O-Al bonds derived from the reaction of an organoaluminum compound and water.

2. A process as claimed in Claim 1 characterised in that said compound (ii) is an organoaluminum compound of the formulae



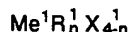
wherein R is a hydrocarbon group having 1-24 carbon atoms and X is a halogen atom.

3. A process as claimed in Claim 1 or Claim 2 characterised in that said inorganic carrier (iv) is formed of a porous inorganic compound of the group consisting of a carbonaceous material, metal, metal oxide, metal chloride, metal carbonate and mixtures thereof, said inorganic carrier having a maximum length of 5-200  $\mu m$ , a surface area of 5-1,000  $m^2/g$  and a pore volume of 0.05-3  $cm^3/g$ .

4. A process as defined in Claim 1 or Claim 2 characterised in that said particulate polymer carrier (iv) is formed of a thermoplastic or thermosetting resin having an average particle size of 5-2,000  $\mu m$ .

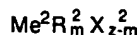
5. A process as claimed in Claim 1 or Claim 2 characterised in that said carrier (iv) is treated with a compound of the group consisting of an active hydrogen-containing compound such as alcohol and aldehydes, an electron-donative compound such as ester and ether and an alkoxide-containing compound such as tetraalkoxysilicate, trialkoxyaluminum and transition-metal tetraalkoxide.

6. A catalyst component for use in the manufacture of polyolefins which is derived from the reaction of a compound (i) of the formula



wherein  $R^1$  is an alkyl, alkoxy, aryloxy or aralkyloxy group of 1-24 carbon atoms,  $X^1$  is a halogen atom;  $Me^1$  is a metal of the group of zirconium, titanium and hafnium, and n is an integer of  $0 \leq n \leq 4$ , in an amount by transition metal concentration of 0.01-500 millimoles per 100g of a carrier (ii) defined hereinafter;

a compound (ii) of the formula



wherein  $R^2$  is a hydrocarbon group of 1-24 carbon atoms,  $X^2$  is an alkoxy group of 1-12 carbon atoms or a halogen atom;  $Me^2$  is an element of Groups I-III in the Periodic Table, z is the valence of  $Me^2$ , and m is an integer of  $0 < m \leq 3$ , in an amount of 0.01-1000 moles per mole of said compound (i);

an organocyclic compound (iii) in an amount of 0.01-100 moles per mole of said compound (i), said organocyclic compound (iii) being selected from the group consisting of cyclic hydrocarbon compounds having two or more conjugated double bond and a carbon number of 4-24 in the molecule; a compound of the formula



wherein Cp is a cyclopentadienyl group,  $R^3$  is a hydrocarbon group of 1-24 carbon atoms,  $X^3$  is a halogen atom,

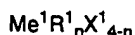
and r and s are  $0 < r \leq 4$  and  $0 \leq s \leq 3$  respectively; and a compound of the formula



wherein Ind is an indenyl group,  $\text{R}^4$  is a hydrocarbon group of 1-24 carbon atoms,  $\text{X}^4$  is a halogen atom, and t and u are  $0 < t \leq 4$  and  $0 \leq u \leq 3$  respectively; and an inorganic carrier and/or particulate polymer carrier (iv).

#### Patentansprüche

- Verfahren zur Herstellung von Polyolefinen, das das Polymerisieren eines olefinischen Kohlenwasserstoffs, ausgewählt aus der Gruppe, die aus alpha-Olefinen, cyclischen Olefinen, Dienen, Trienen und Styrolanalogen besteht, in Anwesenheit einer Katalysatorzusammensetzung umfaßt, wobei die Katalysatorzusammensetzung einen ersten Bestandteil (I) und einen zweiten Bestandteil (II) umfaßt, wobei der erste Bestandteil (I) erhalten wird aus der Umsetzung einer Verbindung (i) der Formel



wobei  $\text{R}^1$  eine Alkyl-, Alkoxy-, Aryloxy- oder Aralkyloxygruppe von 1-24 Kohlenstoffatomen ist,  $\text{X}^1$  ein Halogenatom ist,  $\text{Me}^1$  ein Metall aus der Gruppe von Zirkonium, Titan und Hafnium ist und n eine ganze Zahl von  $0 \leq n \leq 4$  ist, in einer Menge entsprechend einer Konzentration des Übergangsmetalls von 0,01-500 Millimol pro 100 g eines nachstehend definierten Trägers (iv);

einer Verbindung (ii) der Formel  $\text{Me}^2 \text{R}_m^2 \text{X}_{z-m}^2$  wobei  $\text{R}^2$  eine Kohlenwasserstoffgruppe von 1-24 Kohlenstoffatomen ist,  $\text{X}^2$  eine Alkoxygruppe von 1-12 Kohlenstoffatomen oder ein Halogenatom ist,  $\text{Me}^2$  ein Element der Gruppen I-III im Periodensystem ist, z die Wertigkeit von  $\text{Me}^2$  ist und m eine ganze Zahl von  $0 < m \leq z$  ist, in einer Menge von 0,01-100 Mol pro Mol der Verbindung (i);

einer cycloorganischen Verbindung (iii) in einer Menge von 0,01-10 Mol pro Mol der Verbindung (i), wobei die cycloorganische Verbindung aus der Gruppe ausgewählt ist, die aus cyclischen Kohlenwasserstoffen mit 2 oder mehr konjugierten Doppelbindungen im Molekül und einer Kohlenstoffanzahl von 4-24 besteht; einer Verbindung der Formel



wobei Cp eine Cyclopentadienylgruppe ist,  $\text{R}^3$  eine Kohlenwasserstoffgruppe von 1-24 Kohlenstoffatomen ist,  $\text{X}^3$  ein Halogenatom ist und r und s  $0 < r \leq 4$  bzw.  $0 \leq s \leq 3$  sind, und einer Verbindung der Formel



wobei Ind eine Indenylgruppe ist,  $\text{R}^4$  eine Kohlenwasserstoffgruppe von 1-24 Kohlenstoffatomen ist,  $\text{X}^4$  ein Halogenatom ist; und t und u  $0 < t \leq 4$  bzw.  $0 \leq u \leq 3$  sind; und

eines anorganischen Trägers und/oder teilchenförmigen polymeren Trägers (iv);

wobei der zweite Bestandteil (II) eine modifizierte aluminiumorganische Verbindung mit Al-O-Al-Bindungen ist, die aus der Umsetzung einer aluminiumorganischen Verbindung und Wasser erhalten wird.

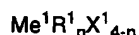
- Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Verbindung (ii) eine aluminiumorganische Verbindung der Formeln



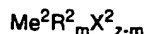
ist, wobei R eine Kohlenwasserstoffgruppe mit 1-24 Kohlenstoffatomen ist und X ein Halogenatom ist.

- Verfahren nach Anspruch 1 oder Anspruch 2, dadurch gekennzeichnet, daß der anorganische Träger (iv) aus einer porösen anorganischen Verbindung der Gruppe, die aus einem kohlenstoffhaltigen Material, Metall, Metalloxid, Metallchlorid, Metallcarbonat und Gemischen davon besteht, erzeugt wird, wobei der anorganische Träger eine maximale Länge von 5-200  $\mu\text{m}$ , eine Oberfläche von 5-1000  $\text{m}^2/\text{g}$  und ein Porenvolumen von 0,05-3  $\text{cm}^3/\text{g}$  aufweist.

4. Verfahren nach Anspruch 1 oder Anspruch 2, dadurch gekennzeichnet, daß der teilchenförmige polymere Träger (iv) aus einem thermoplastischen oder wärmehärtbaren Harz mit einer mittleren Teilchengröße von 5-2000 µm erzeugt wird.
5. Verfahren nach Anspruch 1 oder Anspruch 2, dadurch gekennzeichnet, daß der Träger (iv) mit einer Verbindung aus der Gruppe, die aus einer aktiven Wasserstoff enthaltenden Verbindung, wie z.B. Alkohol und Aldehyde, einer Elektronen abgebenden Verbindung, wie z.B. Ester und Ether, und einer Alkoxid enthaltenden Verbindung, wie z.B. Tetraalkoxysilicat, Trialkoxyaluminium und Übergangsmetalltetraalkoxid, besteht, behandelt wird.
6. Katalysatorbestandteil zur Verwendung bei der Herstellung von Polyolefinen, der erhalten wird aus der Umsetzung einer Verbindung (i) der Formel



- wobei  $\text{R}^1$  eine Alkyl-, Alkoxy-, Aryloxy- oder Aralkyloxygruppe von 1-24 Kohlenstoffatomen ist,  $\text{X}^1$  ein Halogenatom ist;  $\text{Me}^1$  ein Metall aus der Gruppe von Zirkonium, Titan und Hafnium ist, und  $n$  eine ganze Zahl von  $0 \leq n \leq 4$  ist, in einer Menge entsprechend einer Konzentration des Übergangsmetalls von 0,01-500 Millimol pro 100 g eines nachstehend definierten Trägers (iv);  
einer Verbindung (ii) der Formel



- wobei  $\text{R}^2$  eine Kohlenwasserstoffgruppe von 1-24 Kohlenstoffatomen ist,  $\text{X}^2$  eine Alkoxygruppe von 1-12 Kohlenstoffatomen oder ein Halogenatom ist,  $\text{Me}^2$  ein Element der Gruppen I-III im Periodensystem ist,  $z$  die Wertigkeit von  $\text{Me}^2$  ist und  $m$  eine ganze Zahl von  $0 < m \leq 3$  ist, in einer Menge von 0,01-1000 Mol pro Mol der Verbindung (i);  
einer cycloorganischen Verbindung (iii) in einer Menge von 0,01-100 Mol pro Mol der Verbindung (i), wobei die cycloorganische Verbindung (iii) aus der Gruppe ausgewählt ist, die aus cyclischen Kohlenwasserstoffverbindungen mit 2 oder mehr konjugierten Doppelbindungen und einer Kohlenstoffanzahl von 4-24 im Molekül besteht;  
einer Verbindung der Formel



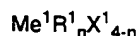
- wobei Cp eine Cyclopentadienylgruppe ist,  $\text{R}^3$  eine Kohlenwasserstoffgruppe von 1-24 Kohlenstoffatomen ist,  $\text{X}^3$  ein Halogenatom ist und  $r$  und  $s$   $0 < r \leq 4$  bzw.  $0 \leq s \leq 3$  sind; und einer Verbindung der Formel



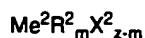
- wobei Ind eine Indenylgruppe ist,  $\text{R}^4$  eine Kohlenwasserstoffgruppe von 1-24 Kohlenstoffatomen ist,  $\text{X}^4$  ein Halogenatom ist, und  $t$  und  $u$   $0 < t \leq 4$  bzw.  $0 \leq u \leq 3$  sind; und  
eines anorganischen Trägers und/oder teilchenförmigen polymeren Trägers (iv).

## Revendications

1. Procédé pour la fabrication de polyoléfines, qui consiste à polymériser un hydrocarbure oléfinique choisi dans le groupe constitué par les alpha-oléfines, les oléfines cycliques, les diènes, les triènes et les analogues du styrène, en présence d'une composition catalytique, ladite composition catalytique comprenant un premier constituant (I) et un second constituant (II),  
ledit premier constituant (I) résultant de la réaction  
d'un composé (i) de formule



- dans laquelle  $\text{R}^1$  est un groupe alkyle, alkoxy, aryloxy ou aralkyloxy de 1 à 24 atomes de carbone,  $\text{X}^1$  est un atome d'halogène,  $\text{Me}^1$  est un métal du groupe du zirconium, du titane et du hafnium, et  $n$  est un nombre entier de  $0 \leq n \leq 4$ , en une proportion, en concentration en métal de transition, de 0,01 à 500 mmoles pour 100 g d'un support (iv) défini ci-après;  
d'un composé (ii) de formule



dans laquelle  $\text{R}^2$  est un groupe hydrocarboné de 1 à 24 atomes de carbone,  $\text{X}^2$  est un groupe alcoxy de 1 à 12 atomes de carbone ou un atome d'halogène,  $\text{Me}^2$  est un élément des groupes I à III du tableau périodique,  $z$  est la valence de  $\text{Me}^2$ , et  $m$  est un nombre entier de  $0 < m \leq z$ , en une proportion de 0,01 à 100 moles par mole dudit composé (i);

d'un composé organocyclique (iii), en une proportion de 0,01 à 10 moles par mole dudit composé (i), ledit composé organocyclique étant choisi dans le groupe constitué par les hydrocarbures cycliques ayant 2 doubles liaisons conjuguées ou plus dans la molécule et un nombre de carbones de 4 à 24; un composé de formule



dans laquelle  $\text{Cp}$  est un groupe cyclopentadiényle,  $\text{R}^3$  est un groupe hydrocarboné de 1 à 24 atomes de carbone,  $\text{X}^3$  est un atome d'halogène et  $r$  et  $s$  sont  $0 < r \leq 4$  et  $0 \leq s \leq 3$  respectivement, et un composé de formule



dans laquelle  $\text{Ind}$  est un groupe indényle,  $\text{R}^4$  est un groupe hydrocarboné de 1 à 24 atomes de carbone,  $\text{X}^4$  est un atome d'halogène; et  $t$  et  $u$  sont  $0 < t \leq 4$  et  $0 \leq u \leq 3$  respectivement; et

d'un support inorganique et/ou support polymère particulaire (iv);

ledit second constituant (II) étant un composé organoaluminique modifié ayant des liaisons Al-O-Al provenant de la réaction d'un composé organoaluminique et d'eau.

2. Procédé selon la revendication 1, caractérisé en ce que ledit composé (ii) est un composé organoaluminique des formules



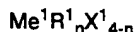
dans lesquelles  $\text{R}$  est un groupe hydrocarboné ayant 1 à 24 atomes de carbone et  $\text{X}$  est un atome d'halogène.

3. Procédé selon la revendication 1 ou la revendication 2, caractérisé en ce que ledit support inorganique (iv) est formé d'un composé inorganique poreux du groupe constitué par une matière carbonée, un métal, un oxyde de métal, un chlorure de métal, un carbonate de métal et des mélanges de ceux-ci, ledit support inorganique ayant une longueur maximale de 5 à 200  $\mu\text{m}$ , une surface spécifique de 5 à 1000  $\text{m}^2/\text{g}$  et un volume de pore de 0,05 à 3  $\text{cm}^3/\text{g}$ .

4. Procédé selon la revendication 1 ou la revendication 2, caractérisé en ce que ledit support polymère particulaire (iv) est formé d'une résine thermoplastique ou thermodurcissable ayant une taille moyenne de particule de 5 à 2000  $\mu\text{m}$ .

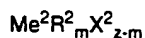
5. Procédé selon la revendication 1 ou la revendication 2, caractérisé en ce que ledit support (iv) est traité avec un composé du groupe constitué par un composé contenant de l'hydrogène actif tel qu'un alcool et les aldéhydes, un composé donneur d'électron tel qu'un ester et un éther, et un composé contenant des groupes alcoxydes tels qu'un silicate de tétraalcoxy, un trialkoxyaluminium et un tétraalcoxyde de métal de transition.

6. Constituant catalytique pour l'utilisation dans la fabrication de polyoléfines, qui provient de la réaction d'un composé (i) de formule



dans laquelle  $\text{R}^1$  est un groupe alkyle, alcoxy, aryloxy ou aralkyloxy de 1 à 24 atomes de carbone,  $\text{X}^1$  est un atome d'halogène,  $\text{Me}^1$  est un métal du groupe du zirconium, du titane et du hafnium, et  $n$  est un nombre entier de  $0 \leq n \leq 4$ , en une proportion, en concentration en métal de transition, de 0,01 à 500 mmoles pour 100 g d'un support (iv) défini ci-après;

d'un composé (ii) de formule



dans laquelle  $R^2$  est un groupe hydrocarboné de 1 à 24 atomes de carbone,  $X^2$  est un groupe alcoxy de 1 à 12 atomes de carbone ou un atome d'halogène;  $Me^2$  est un élément des groupes I à III du tableau périodique,  $z$  est la valence de  $Me^2$ , et  $m$  est un nombre entier de  $0 < m \leq 3$ , en une proportion de 0,01 à 1000 moles par mole dudit composé (i);

d'un composé organocyclique (iii), en une proportion de 0,01 à 100 moles par mole dudit composé (i), ledit composé organocyclique (iii) étant choisi dans le groupe constitué par les composés hydrocarbonés cycliques ayant 2 doubles liaisons conjuguées ou plus et un nombre de carbones de 4 à 24 dans la molécule; un composé de formule



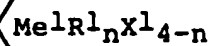
dans laquelle Cp est un groupe cyclopentadiényle,  $R^3$  est un groupe hydrocarboné de 1 à 24 atomes de carbone,  $X^3$  est un atome d'halogène et  $r$  et  $s$  sont  $0 < r \leq 4$  et  $0 \leq s \leq 3$  respectivement, et un composé de formule



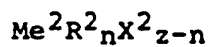
dans laquelle Ind est un groupe indényle,  $R^4$  est un groupe hydrocarboné de 1 à 24 atomes de carbone,  $X^4$  est un atome d'halogène; et  $t$  et  $u$  sont  $0 < t \leq 4$  et  $0 \leq u \leq 3$  respectivement; et d'un support inorganique et/ou support polymère particulaire (iv).

FIG. 1

transition metal component (I)



$\text{Me}^1 = \text{Zr, Ti or Hf}$



$\text{Me}^2 = \text{I - III groups}$

organic compound having  
2 or more cyclic conjugated  
double bonds

inorganic carrier and/or  
particulate polymer carrier

organometal component (II)

modified organoaluminum compound  
having Al-O-Al bonds

Olefins